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MEMORANDUM FOR PRS (Contractor Publication)

19 May 2003

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5364 Boatz, Jerry (PRSP), "New Materials Design"

DoD High Performance Computing Users Group Conference **(Statement A)**
(Bellevue, WA, 9-13 Jun 2003) (Deadline = 9 Jun 2003)

New Materials Design

DoD UGC, 9-13 June 2003

Bellevue, WA

Jerry Boatz

Senior Research Chemist

Propulsion Directorate

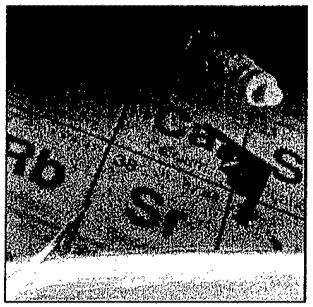
Air Force Research Laboratory

NEW MATERIALS DESIGN

THE TEAM....

Prof. Mark S. Gordon

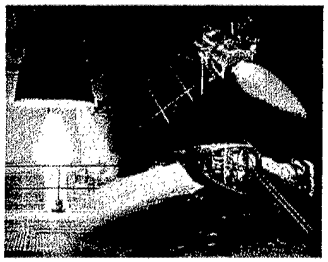
Dr. Ruth Pachter, AFRL/MLPJ



Prof. Gregory Voth

THE UNIVERSITY OF UTAH

Dr. Jerry Boatz, AFRL/PRSP



Prof. Sharon Hammes-Schiffer

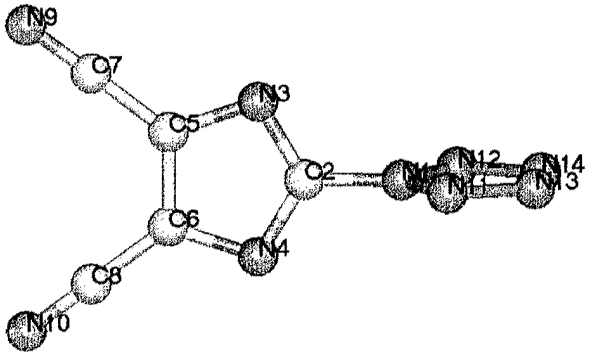
PENNSTATE

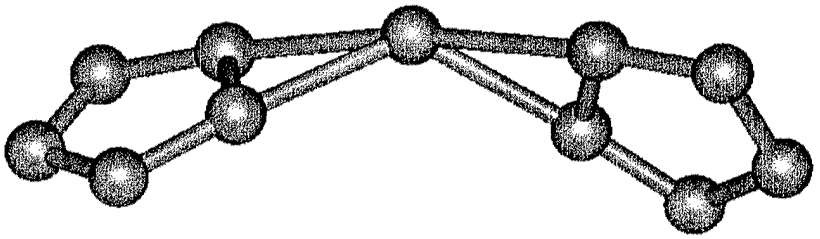
OUTLINE

1. **Project Overview**
   - High energy density materials
   - Polyhedral oligomeric silsesquioxanes (POSS)
   - Non-linear optical materials
2. **Theoretical Methods and benchmarks**
   - Ab initio electronic structure theory
   - Nuclear-electronic orbital approach
3. **Results**
4. **Summary**

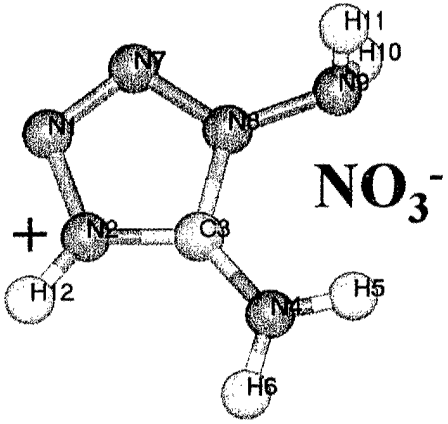
PROJECT OVERVIEW - HEDM

High Energy Density Matter -- next generation rocket propellants





High-nitrogen/polynitrogen compounds



NO_3^-

Energetic Ionic Liquids

Specific Impulse

$$I_{sp} \propto \sqrt{\Delta H / m}$$

PROJECT OVERVIEW - HEDM

Technical issues being addressed using CCM

1. High-nitrogen/polynitrogen compounds

Objective: identify, characterize, and synthesize stable compounds with high heats of formation, high densities

- geometries, energy content, stabilities, reaction pathways

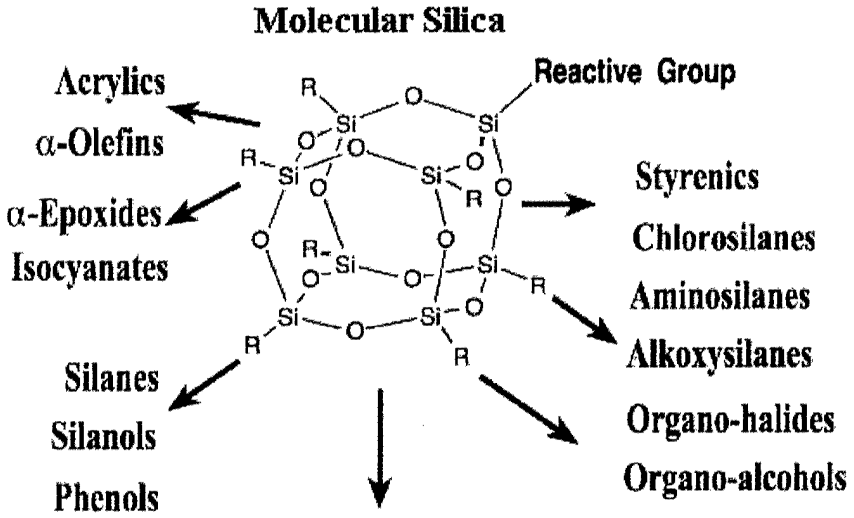
2. Energetic ionic liquids

Objective: identify, characterize, and synthesize thermally stable energetic ILS with low melting points, high densities and low viscosities.

- geometries, electronic structures, stabilities, energy content, interaction potentials

PROJECT OVERVIEW - POSS

Polyhedral oligomeric silsesquioxanes -- next generation plastics



As Additives

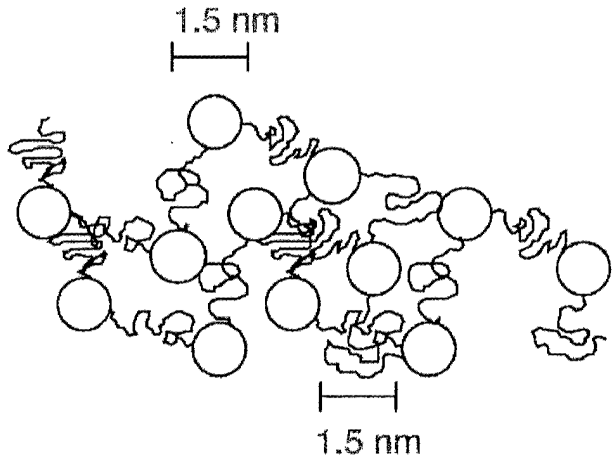
Heat/abrasion resistant paints and coatings
Mechanical property/viscosity/thermal modifiers
Crosslinking agents
Fire retardants

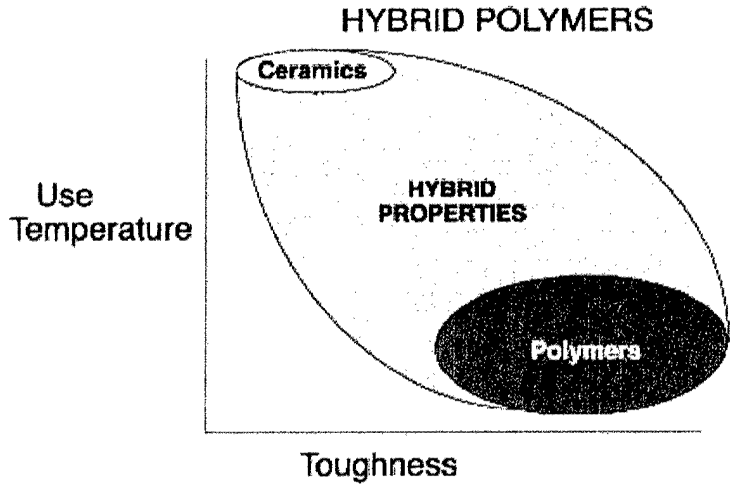
As Plastics

Medical materials
Space resistant resins
Packaging/coatings
Electronic materials
Optical Plastics

As Preceramics

Ablative materials (nozzles, insulations etc.)
Claddings/electronics coatings
Precursors to glassy or ceramic matrices





PROJECT OVERVIEW - POSS

Technical issues being addressed using CCM

1. Mechanisms of formation

Objective: rational design and synthesis of POSS

- role of solvents, acid/base catalysis, substituent effects on mechanism of formation

2. Potential applications as molecular "sieves"

Objective: determine if POSS cages can be used to separate small molecules

- determine barriers to encapsulation of N_2 and O_2

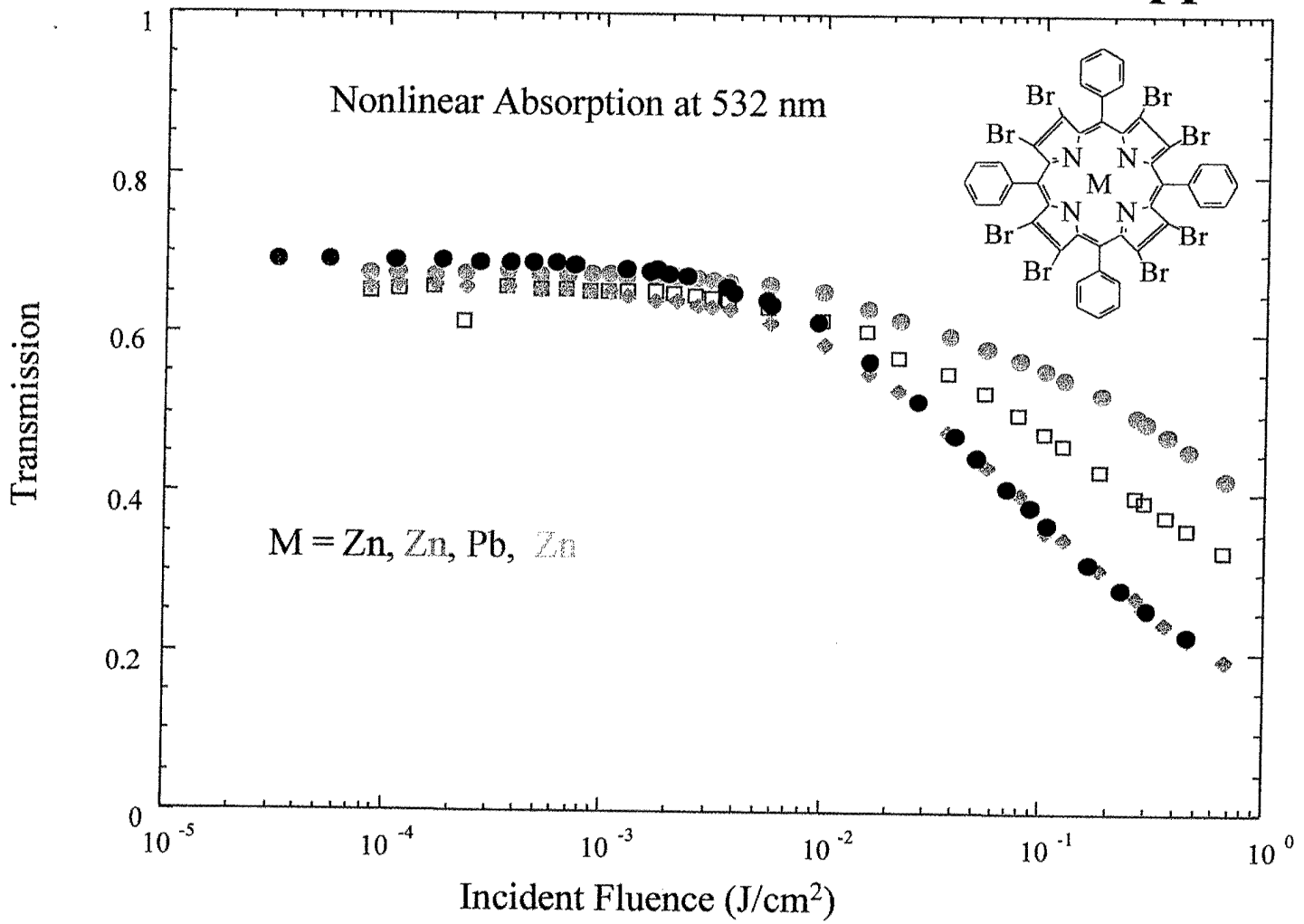
3. Ti-POSS as new catalysts

Objective: determine if Ti-POSS and Ti-siloxane compounds are effective catalysts

- determine barriers to polymerization of ethylene, oxidation by HOOH.

PROJECT OVERVIEW - NLO

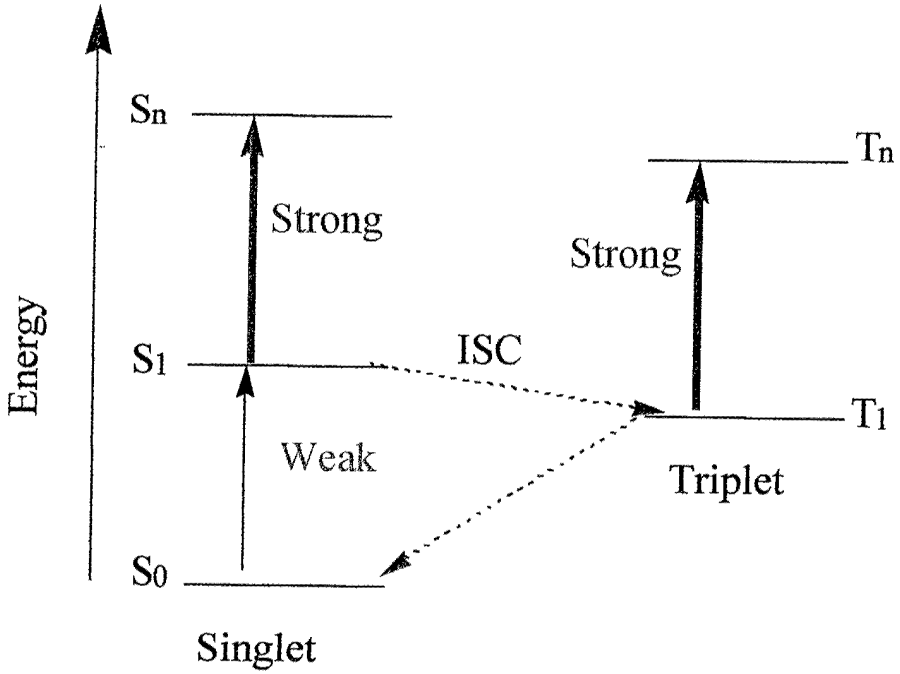
Non-linear optical materials for laser-hardened applications



PROJECT OVERVIEW - NLO

Technical issues being addressed using CCM

1. Mechanism of reverse saturable absorption (RSA)



Five-level model for nonlinear absorption

Key Components of RSA

- **Ground state spectra (linear response)**
- **Singlet-triplet splittings (ISC, phosphorescence)**
- **Ionization potential (photoionization)**
- **Excited triplet spectra (NLA)**

THEORETICAL METHODS

1. **Ab initio electronic structure theory**

   - General Atomic and Molecular Electronic Structure System (GAMESS) -- a CHSSI code

   - Nuclear-electronic orbital approach (NEO) for including nuclear quantum effects (important, e.g., in proton transfer reactions)

Various computational techniques are employed to solve the molecular electronic Schrödinger equation from quantum mechanics:

$$\left[-\frac{1}{2}\sum_i \nabla_i^2 - \sum_i\sum_\alpha \frac{Z_\alpha}{r_{i\alpha}} + \sum_i\sum_{j>i}\frac{1}{r_{ij}}\right]\Psi_{el} = E_{el}\Psi_{el}$$

Categories of approximate solutions:

a) "Self-consistent field" (SCF): reasonably good geometries
b) "Electron correlation": post-SCF correction, required for reliable energetics (e.g., barriers).

THEORETICAL METHODS

1. **Ab initio electronic structure theory (cont.)**

- Most electronic structure codes use Born-Oppenheimer (i.e., "clampled nuclei") approximation -- NOE method treats specified nuclei at QM level.

Nuclear-Electronic Hamiltonian

$$
\begin{aligned}
H_{\mathrm{tot}}(\mathbf{r}_e, \mathbf{r}_q; \mathbf{r}_c) \;=\; & -\sum_{i}^{N_e} \frac{1}{2}\nabla_i^2 - \sum_{i}^{N_e}\sum_{A}^{N_c} \frac{Z_A}{r_{iA}} + \sum_{i}^{N_e}\sum_{j>i}^{N_e} \frac{1}{r_{ij}} \\
& - \sum_{I}^{N_p} \frac{1}{2M_I}\nabla_I^2 + \sum_{I}^{N_p}\sum_{A}^{N_c} \frac{Z_A Z_I}{r_{IA}} + \sum_{I}^{N_p}\sum_{J>I}^{N_p} \frac{Z_I Z_J}{r_{IJ}} \\
& - \sum_{i}^{N_e}\sum_{I}^{N_p} \frac{Z_I}{r_{iI}} + \sum_{A}^{N_c}\sum_{B>A}^{N_c} \frac{Z_A Z_B}{r_{AB}}
\end{aligned}
$$

N_e: number of electrons (coordinates $\mathbf{r}_e$)
N_p: number of quantum nuclei (coordinates $\mathbf{r}_p$)
N_c: number of classical nuclei (coordinates $\mathbf{r}_c$)

THEORETICAL METHODS

Ab initio electronic structure theory

Current Status of parallel GAMESS

	RHF	ROHF	UHF	GVB	MCSCF
Energy	cdp	cdp	cdp	cdp	cdp
Analytic Gradient	cdp	cdp	cdp	cdp	cdp
Numeric Hessian	cdp	cdp	cdp	cdp	cdp
Analytic Hessian	cdp	cdp	-	cdp	-
MP2 energy	cdp	cdp	cdp	-	c p
MP2 gradient	cdp	-	cd	-	-
CI energy	cdp	cdp	-	cdp	cdp
CI gradient	cd	-	-	-	-
DFT energy	cdp	cdp	cdp	-	-
DFT gradient	cdp	cdp	cdp	-	-

c = conventional disk storage of AO integrals

d = direct evaluation of AO integrals

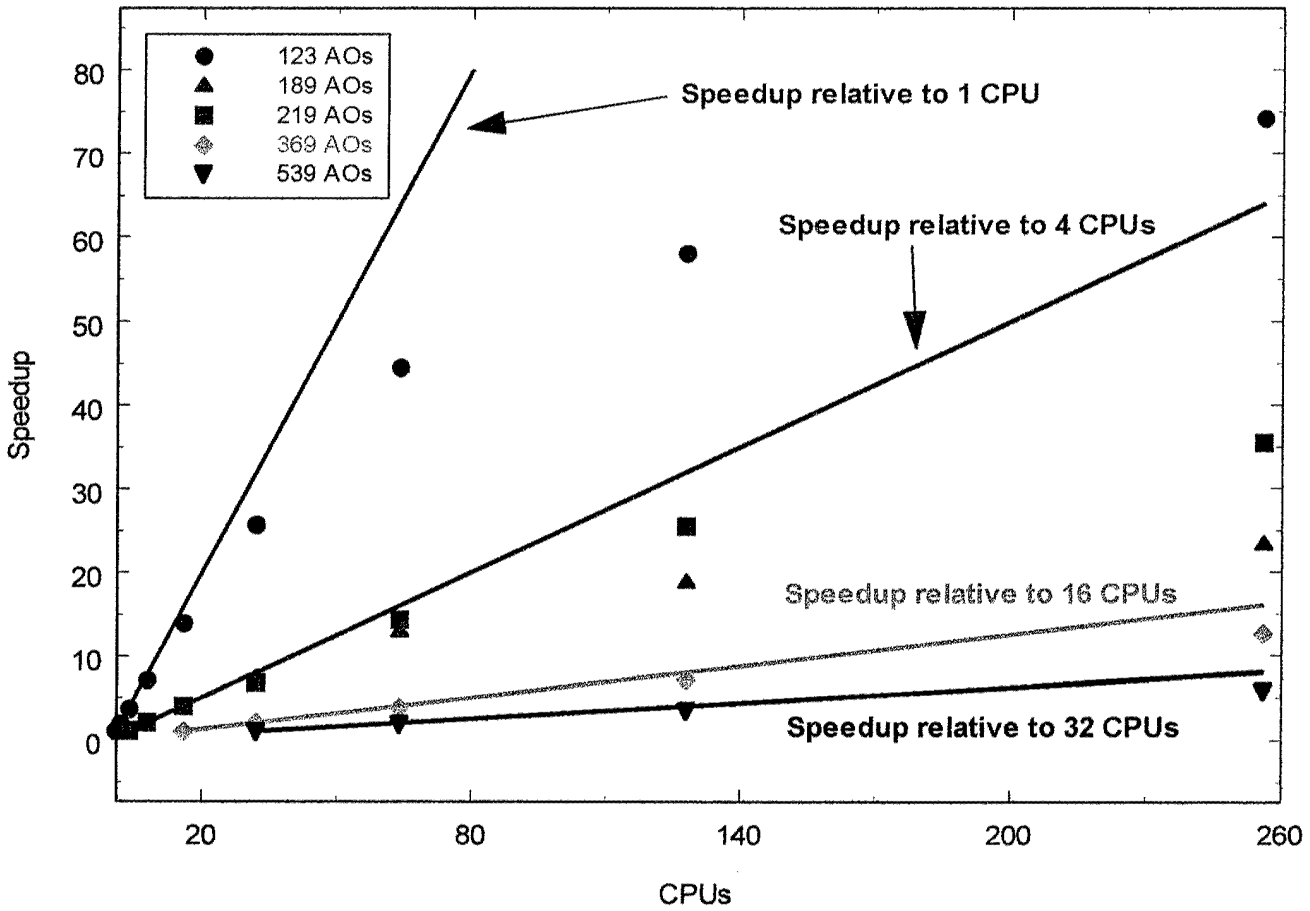
p = runs in parallel

THEORETICAL METHODS

Ab initio electronic structure theory

MP2 Gradient Scalability Test

Silicocene molecule, Si(C5H5)2



The Search for New Polynitrogens

- All polynitrogens are unstable with respect to N_2 molecules
- Their activation energy for N_2 elimination is largely determined by the weakest bond in the compound
- Their metastability is enhanced if suitable resonance structures exist:

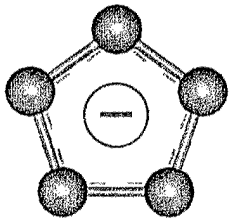
$$[\,|\underline{\overline{N}}\text{–}N\equiv N|\,]^- \longleftrightarrow [\,\langle N{=}N{=}N\rangle\,]^- \longleftrightarrow [\,|N\equiv N\text{–}\underline{\overline{N}}|\,]^-$$

- The double-bond character of the N—N bonds in the azide anion explains its exceptional stability
- How can this stabilization effect be used to our advantage in preparing new compounds?

Pentazolate (N_5^-)?

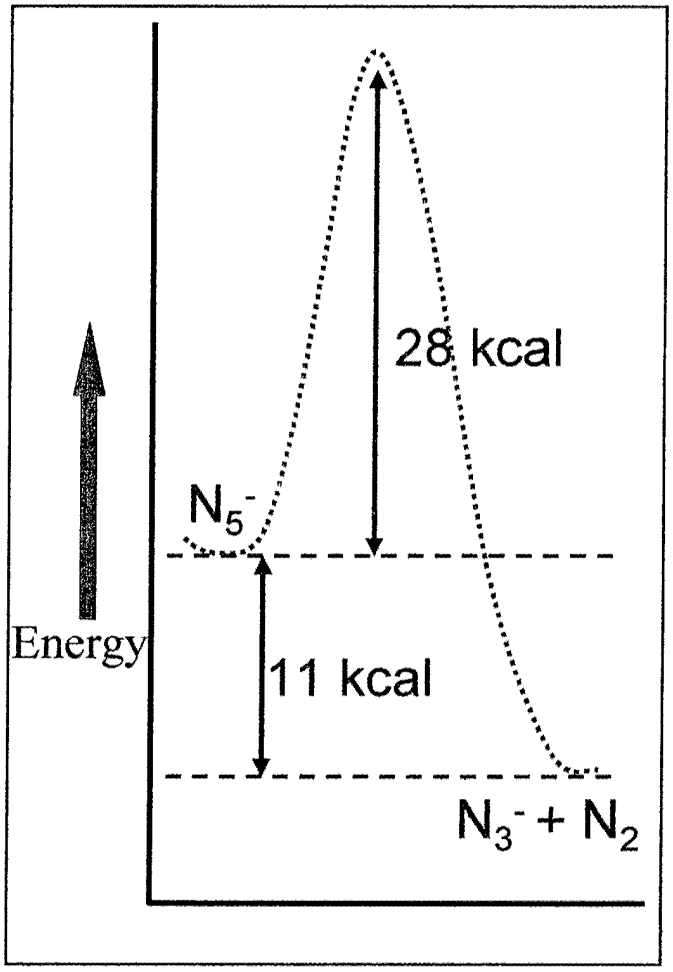
- Substituted pentazoles R-N_5 have been known for decades (R=aryl)
- Cyclic N_5^- is aromatic
- Conversion of the diazonium salt, RN_2^+, to the substituted pentazole ring R-N_5 by the reaction with azide ion, N_3^-, has been demonstrated many years ago by Ugi and Huisgen.
- N_5^- has been recently detected in the gas phase for the first time, using collisional fragmentation (electrospray ion mass spectroscopy).
- Can a chemical route to N_5^- be found? (e.g., can a suitable R group be found for the reaction R-N_2^+ + N_3^- -> R-N_5 -> R^+ + N_5^-?

New Polynitrogen Anions



Pentazole anion (N_5^-)

- *Theoretical calculations show that this anion has a 28 kcal/mole activation energy barrier for decomposition and its decomposition to N_3^- and N_2 is only 11 kcal/mol exothermic*
- *Aryl substituted pentazoles can be isolated as stable compounds only if stored at low temperatures. In methanol, these compounds rapidly decompose at room temperature to form aryl azides and N_2 gas*

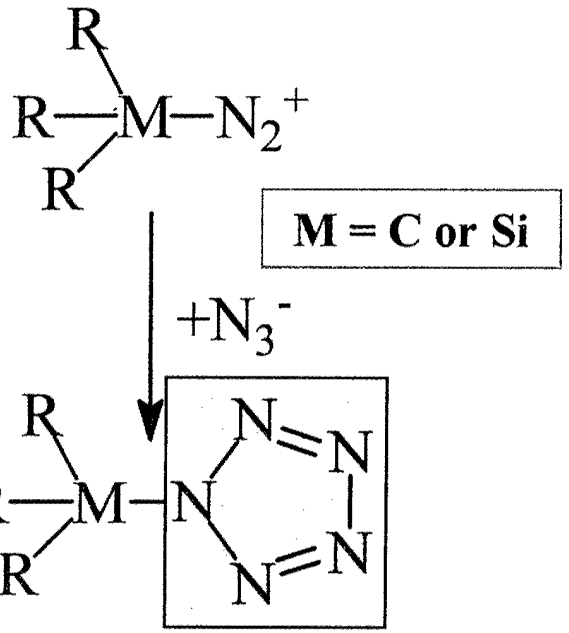


Synthetic Challenge – How do we make These New Anions??

Synthesis of Substituted Pentazoles

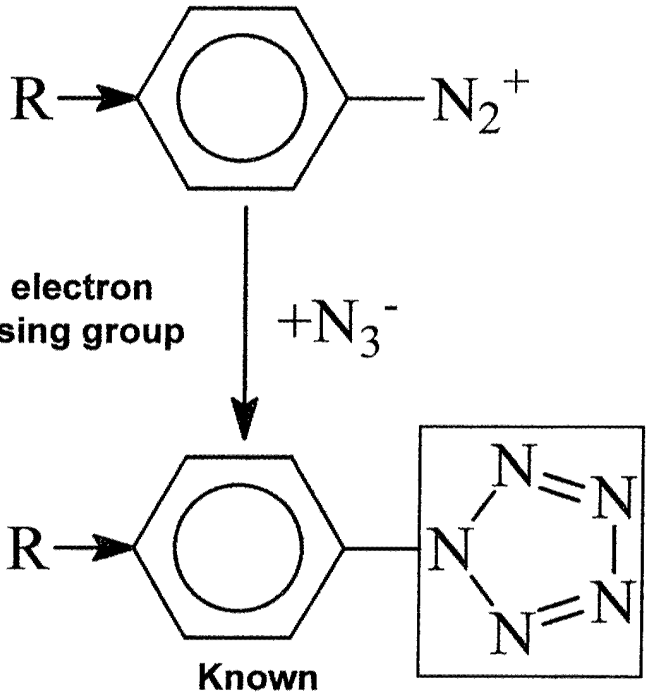
Sources for the Pentazole Anion (N_5^-)

Trityl/Silyl Diazonium Salts



Unknown

Aryl Diazonium Salts



Known

Theoretical Challenge - Can we design and predict viable precursors to N_5^-?

Find a substituent R so that

1. R-N_2^+ is stable wrt $R^+ + N_2$.

2. The R-N bond in R-N_5 is weak, thereby suitable for the reaction R-N_5 + M^+X^- -> $M^+N_5^-$ + R-X

Approach

Use quantum chemical calculations to predict the stability of R-N_2^+ diazonium salts and the length/strength of the R-N_5 bond.

MBPT(2)/6-31G(d) level of theory

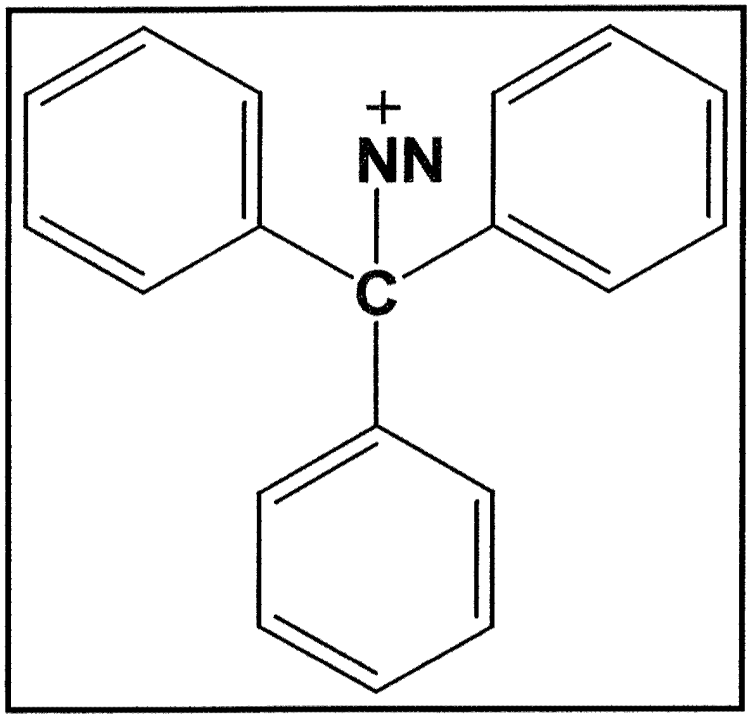
L_3M-N_2^+

M = C, Si

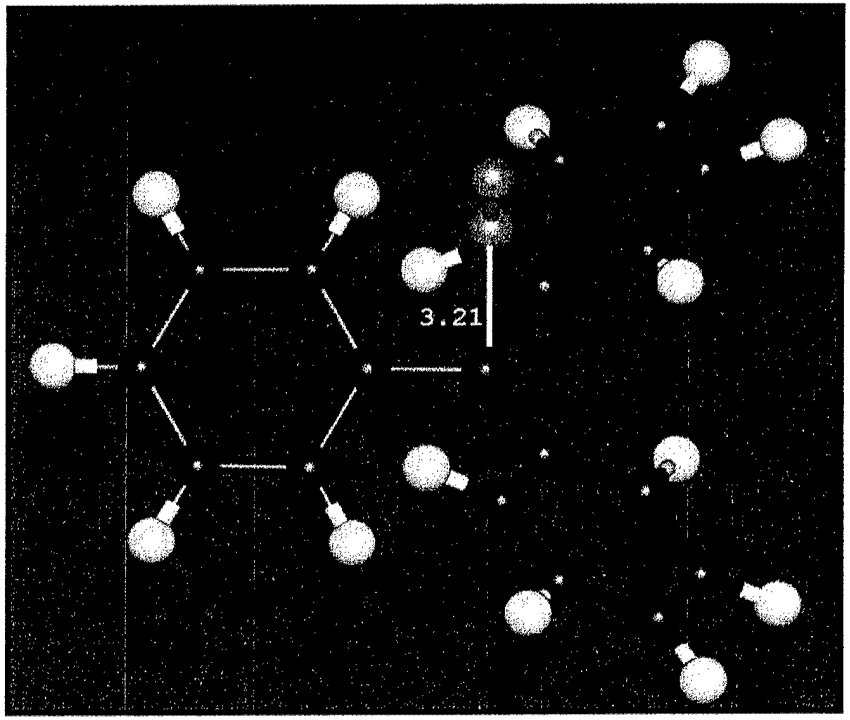
L = F, Cl, CH_3, CF_3, NO_2, phenyl, etc.

Identifying Precursors for New Polynitrogens

This ion has been suggested as a useful precursor to new polynitrogen molecules...



... but calculations predict it to be unstable.

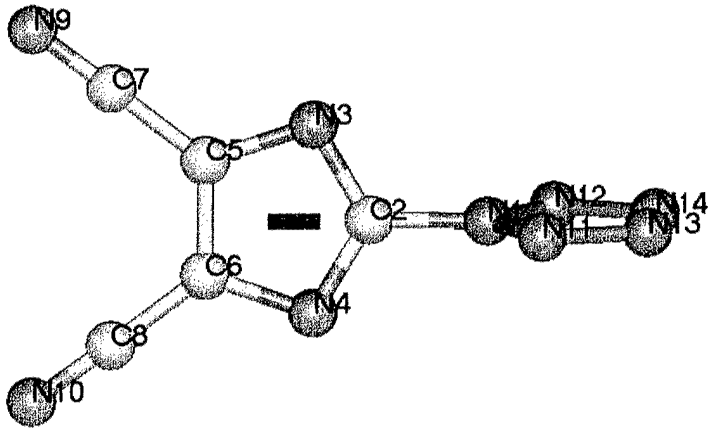


Computational requirements: ~50,000 CPU-hours, 1.2 GW on IBM SP/P3 at ASC

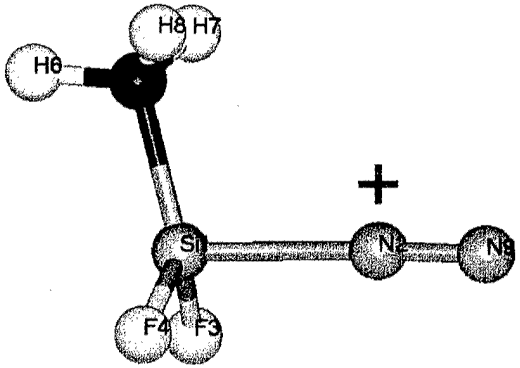
RESULTS - HEDM

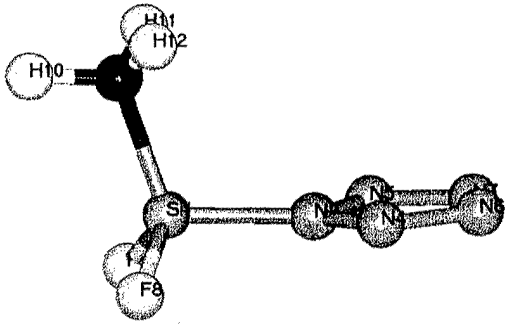
High-nitrogen/polynitrogen compounds

Potential dicyanoimidazolate precursor to displacement of N_5^-



Potential diazonium $[R_3Si\text{-}N_2]^+$ precursors to formation of suitable $R_3Si\text{-}N_5$ substituted pentazoles





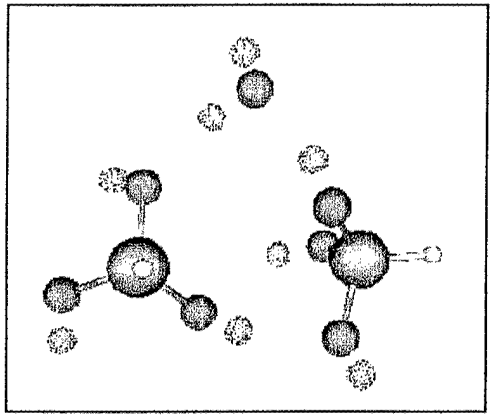
R_3	$R_3Si\text{-}N_2^+$ distance(Å)	$D_e(Si\text{-}N_2^+)$ (kcal/mol)	$R_3Si\text{-}N_5$ distance (Å)
3Me	2.151	13.8	1.855
2Me,F	2.144	15.7	1.834
Me,2F	**2.151**	**21.2**	**1.855**
3F	1.973	33.4	1.783

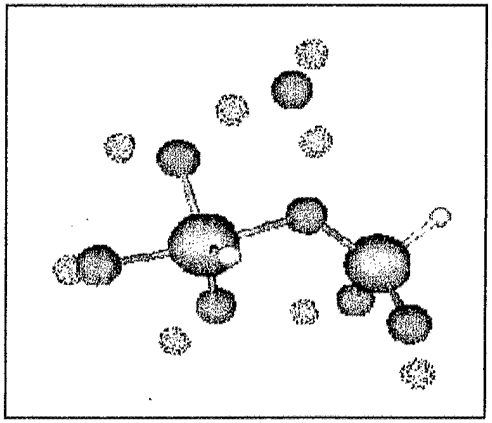
Computational requirements: ~50,000 CPU-hours, 1 GW on IBM SP/P3 at ASC

RESULTS - POSS

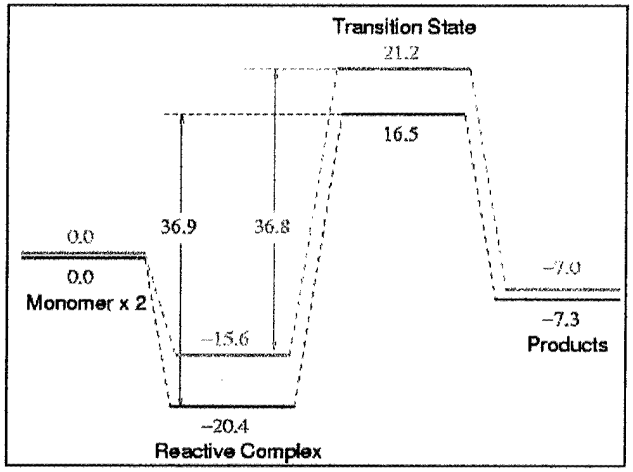
Nuclear quantum effects in water-catalyzed condensation reactions

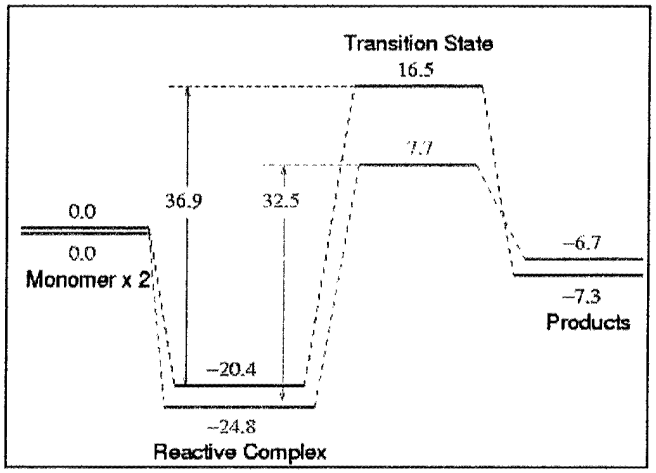
$$2 \times HSi(OH)_3 + H_2O \rightarrow H(OH)_2Si{-}O{-}Si(OH)_2H + 2H_2O$$





Level	Reactive Complex	Transition State	Products	CPU Time
RHF/6-31G*	–20.4	16.5	–7.3	1.0
RHF/6-31G*/ZPE	–15.6	21.2	–7.0	
NEO/HF/4	–23.0	7.2	–5.9	1.1
NEO/HF/8	–24.8	7.7	–6.7	1.8





POSS as catalysts?

Some Ti compounds are know to be effective catalyts
Ziegler-Natta, olefin oxidation

Recent experiments reveal Ti-modified silicates catalyze olefin oxidation by peroxides

Can Ti-substituted siloxanes and/or POSS catalyze olefin oxidation by HOOH, or polymerization?

POSS computational methods

§ B3LYP/6-31G(d) geometry optimizations

§ Hessians to characterize stationary points

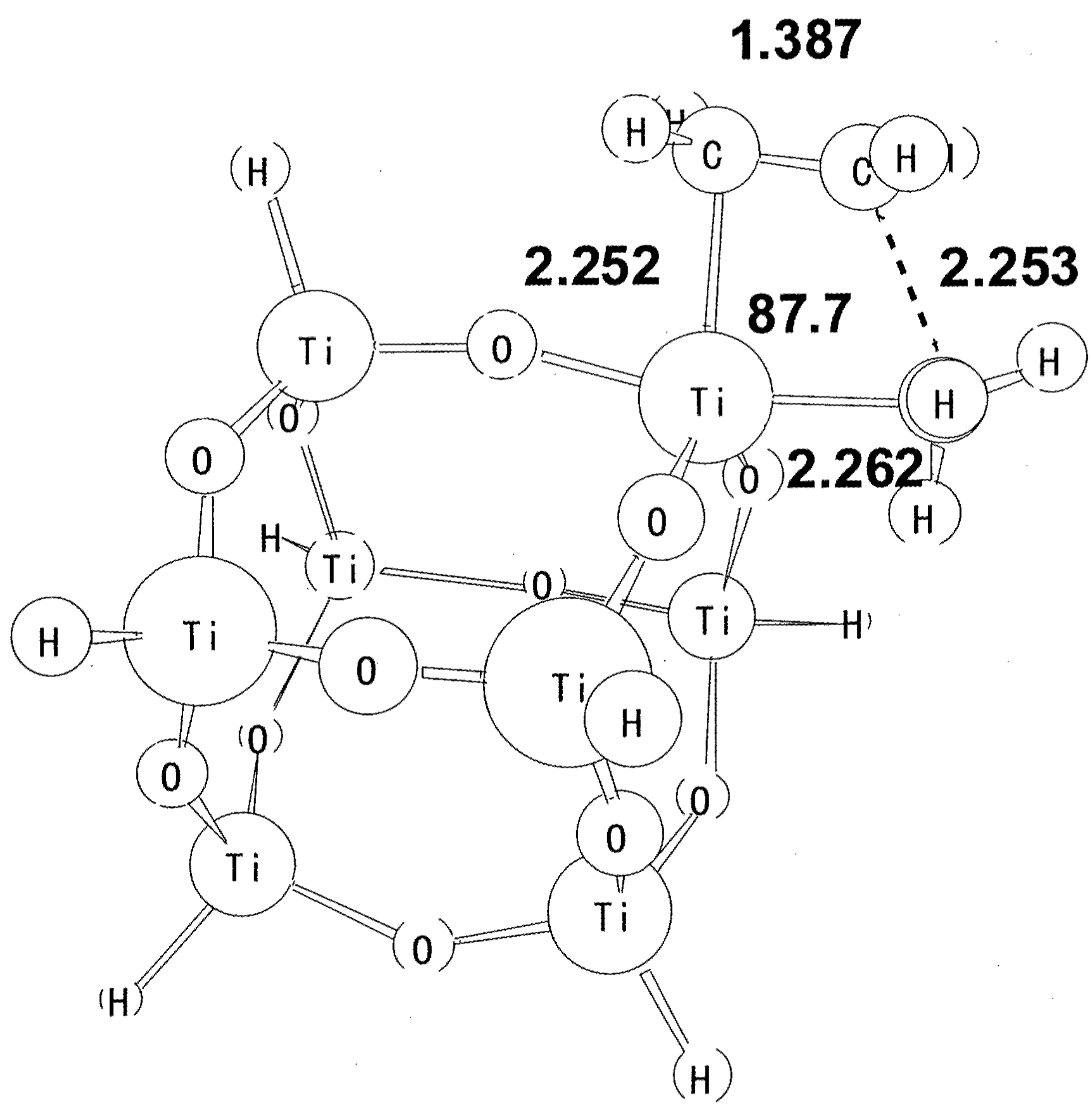
§ Energies using MP2/TZVP

§ Some geometries re-optimized with MP2

§ Size of basis set: ~1,000 basis functions

§ Calculations performed at ERDC (T3E) and AHPCRC (T3E)

TS For Polymerization of Ethylene



RESULTS - NLO

Systematic investigation of excited state energies and oscillator strengths of free-base porphyrins, phthalocyanines, and their metal complexes, representing a broad range of π-conjugated systems, using time-dependent density functional theory (TD-DFT).

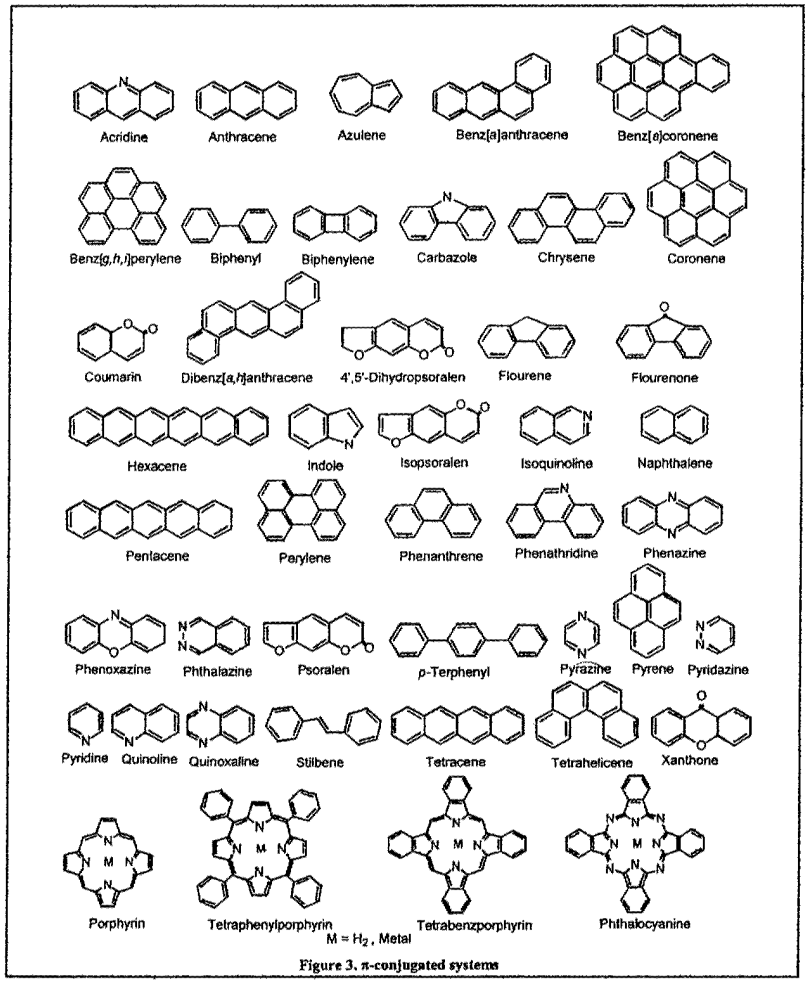
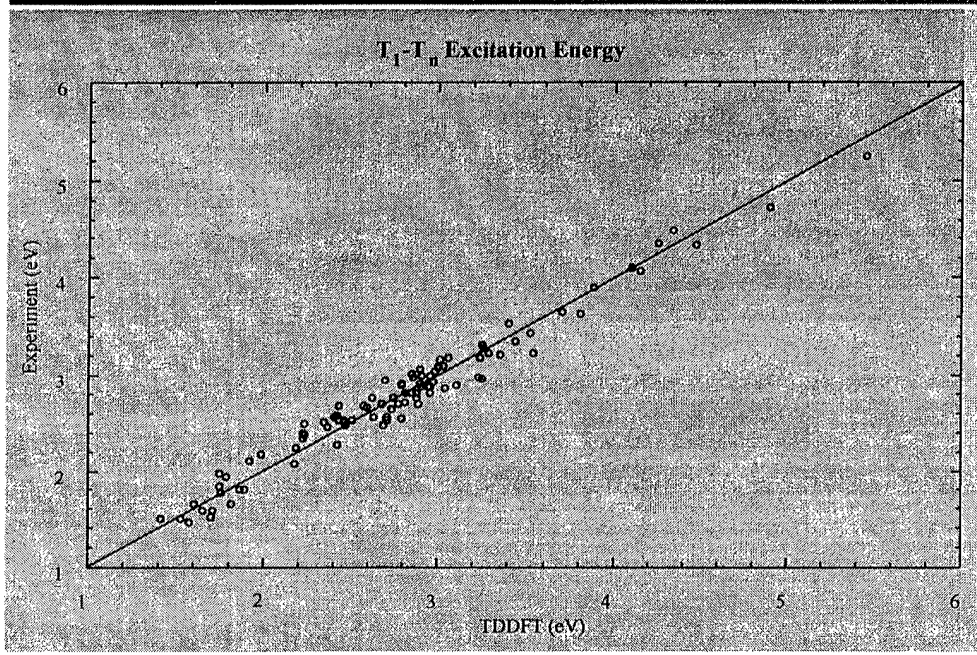
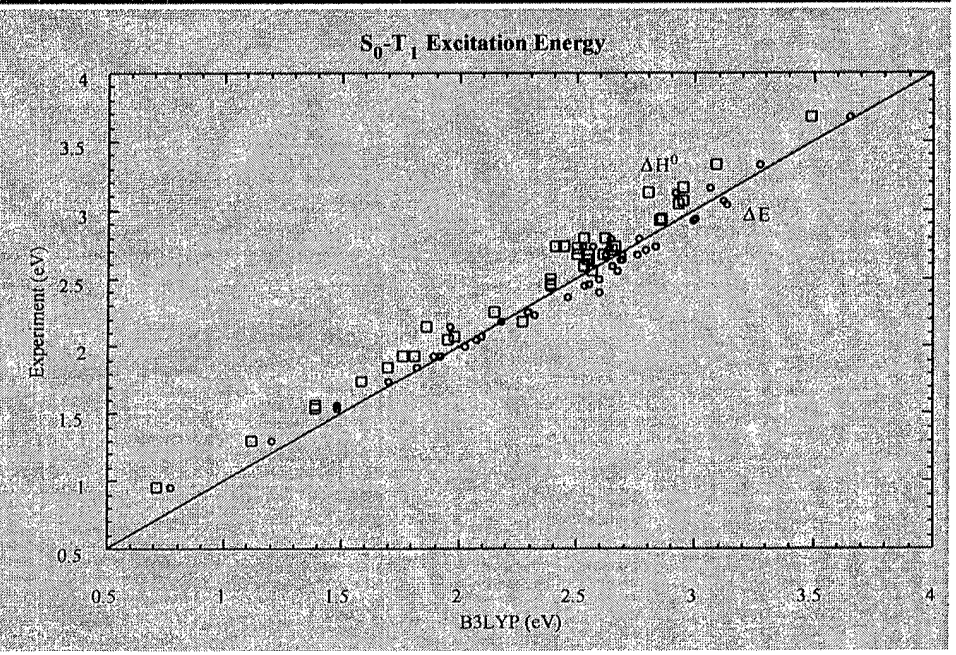


Figure 3. π-conjugated systems

RESULTS - NLO





Computed T_1-T_n compared to experimental results

86 Experimental Values (in solution)
Mean Absolute Error = 0.11
Maximum Error = 0.31

Computed S_0-T_1 compared to experimental results

47 Experimental Values (in solution)
Mean Absolute Error = 0.14
Maximum Error = 0.33

100,000 hours on SGI O2K, Compaq GS320, IBM SP/P3 at ASC

SUMMARY

High Energy Density Matter

- High-nitrogen/polynitrogen compounds are substantially more energetic than hydrazine.
- Trityldiazonium cation is not a stable polynitrogen precursor.
- Trimethylsilyldiazonium cation is marginally stable, replacement of methyls with fluorines increases stability.

Polyhedral Oligomeric Silsesquioxanes (POSS)

- Nuclear quantum effects are important in proton transfer reactions -- lower barriers by about 4 kcal/mol for water-assisted condensation of trisilanol
- Most effective catalyst for olefin polymerization is T_4 cage
- Barrier is still ~10 kcal/mol too high: Ti-POSS, Ti-siloxanes may not be good catalysts for this reaction

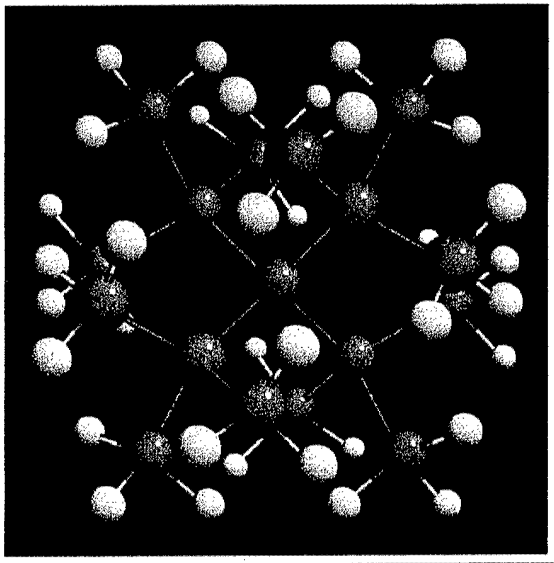
NLO materials

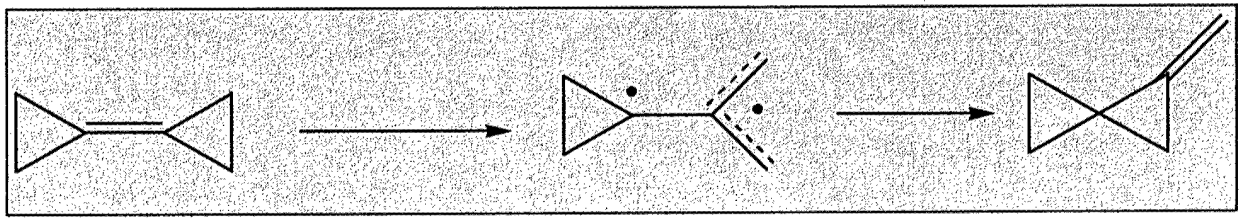
- Time-dependent density functional theory accurately predicts NLA in free-base porphyrins, phthalocyanines, and their metal complexes.
- Mean absolute error of 0.11 eV for computed triplet-triplet excitation energies
- Mean absolute error of 0.14 eV for computed singlet-triplet excitation energies

FUTURE DIRECTIONS

HEDM

- Thermal decomposition mechanisms of energetic hydrocarbons (e.g., BCP).
- Energetic Ionic Liquids (QSPR models)





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MSRCs, DCs: ASC, ARL, ERDC, NAVO, MHPCC, AHPCRC, ARSC, AFFTC

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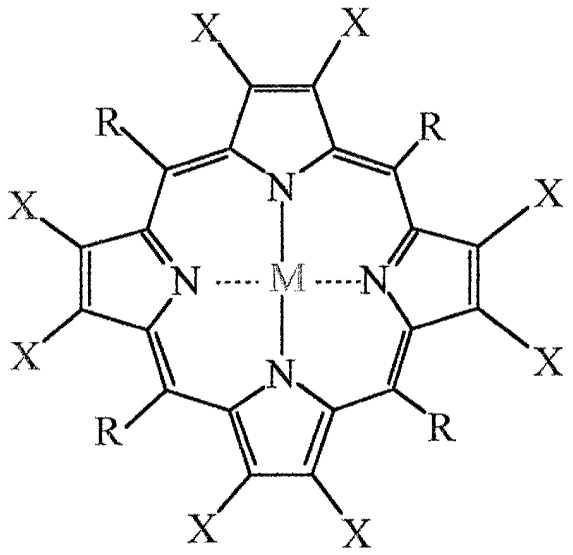
Backup Slides

PROJECT OVERVIEW - NLO

Technical issues being addressed using CCM

2. "Tuning" of absorption spectrum by benzannulation, halide substitution



System				Property			
	M	X	R	IP	S_0-S_n	S_0-T_1	T_1-T_n
PH_2	H_2	**H**	**H**	E, C	E, C	E, C	E, C
ZnP	Zn	**H**	**H**	E, C	E, C	E, C	E, C
$TPPH_2$	Zn	**H**	ϕ	E, C	E, C	E, C	E, C
ZnTPP	Zn	**H**	ϕ	E, C	E, C	E, C	E, C
ZnTPPBr8	Zn	**Br**	ϕ	C	E, C	E, C	E, C

IP = Ionization Potential, S_0 -S_n = Ground State Spectrum,
S_0 -T_1 = Singlet-Triplet Gap T_1 -T_n = Triplet-Triplet Spectrum
E = Experiment, C = Calculated

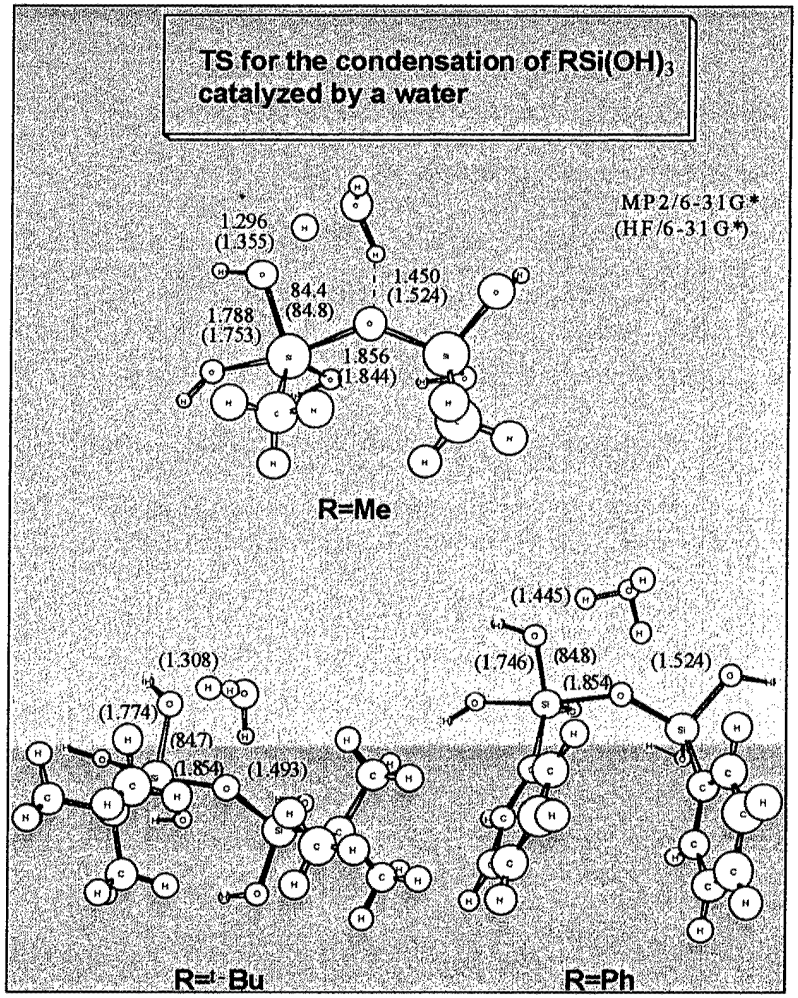
RESULTS - POSS

Mechanism of formation: role of solvent (H_2O) & substituents (R)

$RSi(OH)_3 + RSi(OH)_3 \rightarrow R(OH)_2Si\text{-}O\text{-}Si(OH)_2R + H_2O$

R	Energy barrier (kcal/mol)	
	HF/6-31G*	MP2/6-31G*
H	30.4 (16.7)	10.9 (-9.3)
Me	28.2 (14.7)	7.7 (-13.3)
t-Bu	34.3 (24.9)	9.8 (-9.3)
Ph	31.1 (18.2)	7.9 (-16.4)

Values in parentheses are for water-catalyzed results.



Kudo, T., Gordon, M.S. J. Am. Chem. Soc., 120, 11432 (1998)
Kudo, T., Gordon, M.S. J. Phys. Chem. A, 104, 4058 (2000)

RESULTS - POSS

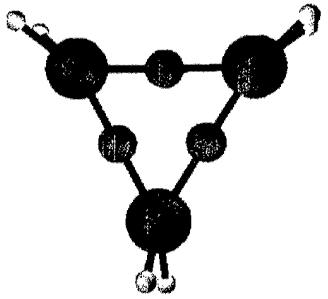
Mechanism of formation

Key steps

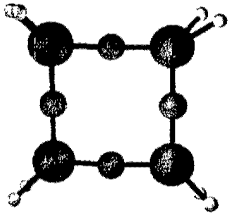
1. Hydrolysis of $RSiX_3$ (R=H,CH_3,t-butyl,etc.; X=Cl)
   $RSiCl_3 + H_2O \rightarrow RSiCl_2OH + HCl$
   $RSiCl_2OH + H_2O \rightarrow RSiCl(OH)_2 + HCl$
   $RSiCl(OH)_2 + H_2O \rightarrow RSi(OH)_3$
2. Condensation of $RSi(OH)_3$ to disiloxane
   $2\ RSi(OH)_3 \rightarrow R(OH)_2SiOSi(OH)_2R + H_2O$
3. Condensation of disiloxane to D_3,D_4
   $RSi(OH)_3 + R(OH)_2SiOSi(OH)_2R \rightarrow D_3 + 2H_2O$

   [2+2]: $2R(OH)_2SiOSi(OH)_2R \rightarrow D_4 + 2H_2O$
   [3+1]: $RSi(OH)_3 + R(OH)_2SiOSi(OH)_2R \rightarrow D_4 + 2H_2O$
   Ring Expansion: $RSi(OH)_3 + D_3 \rightarrow D_4 + H_2O$
4. Condensation of D_3, D_4 to POSS (in progress)
   $2D_4 \rightarrow T_8 + 4H_2O$
   ....

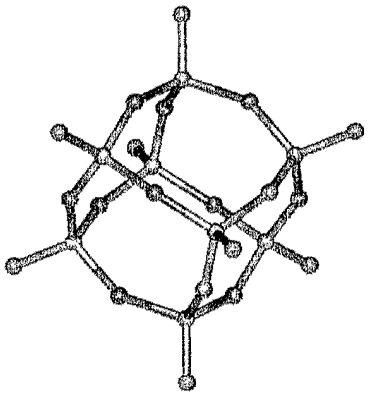
D3



D4

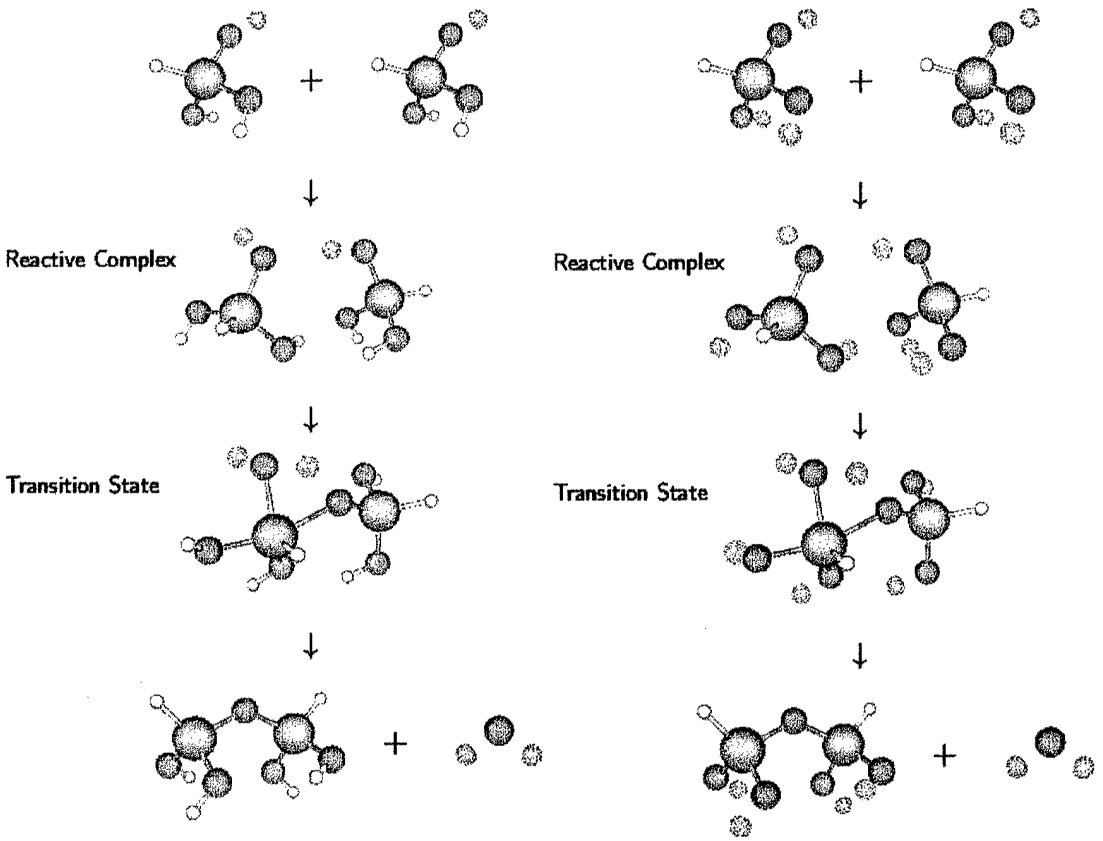


T8



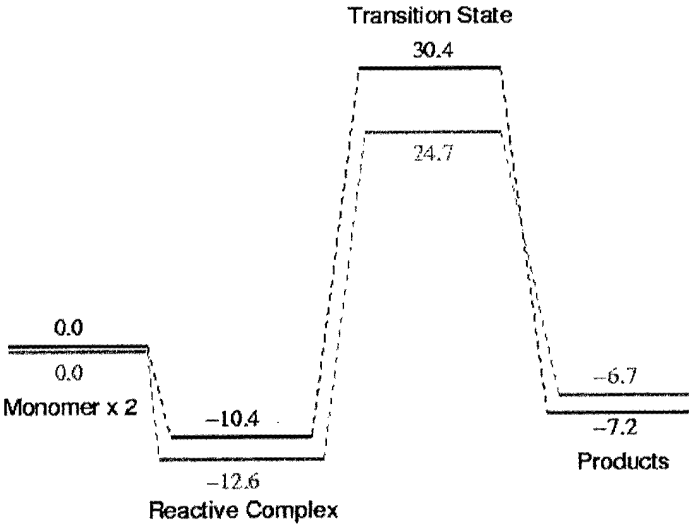
RESULTS - POSS

Nuclear quantum effects in condensation reactions



Level	Monomer × 2	Reactive Complex	Transition State	Products	CPU Time
RHF/6-31G*	0.0	−10.4	30.4	−7.2	1.0
NEO-HF/2	0.0	−11.4	24.9	−5.9	1.1
NEO-HF/6	0.0	−12.6	24.7	−6.7	1.8

Units in kcal/mol



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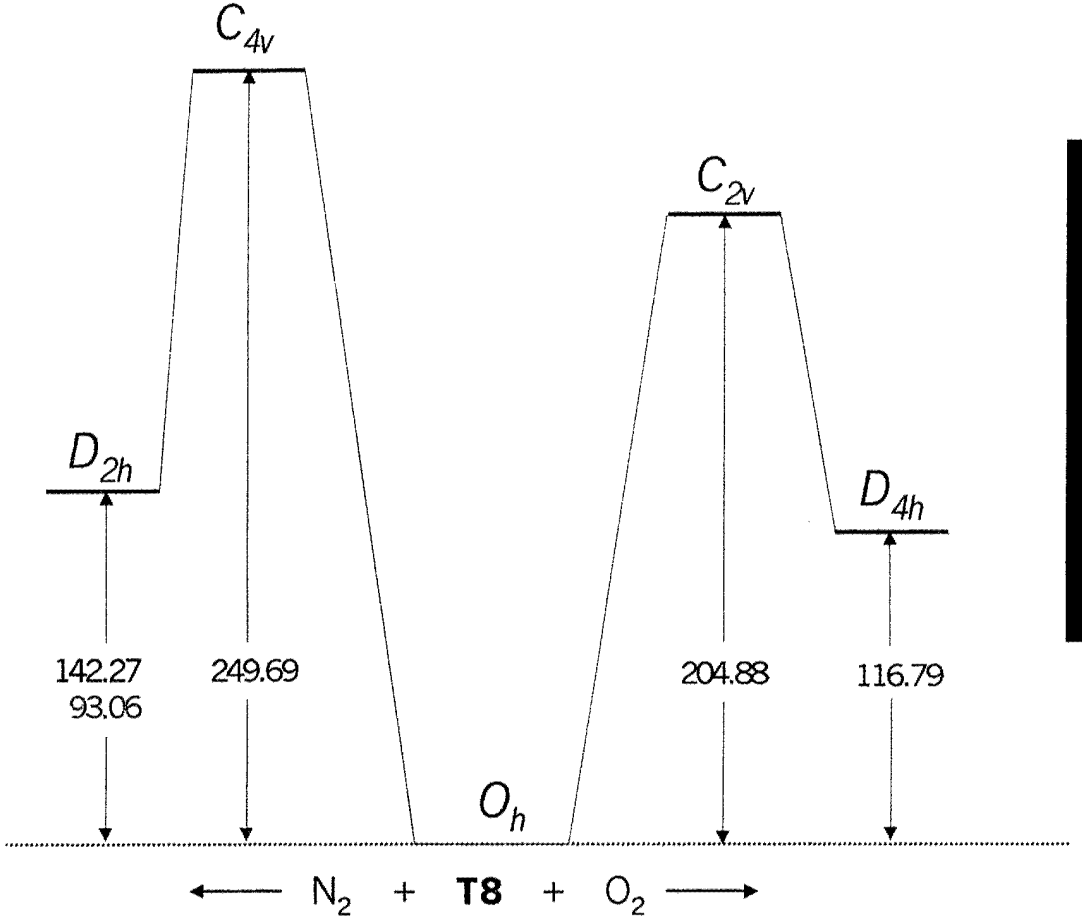
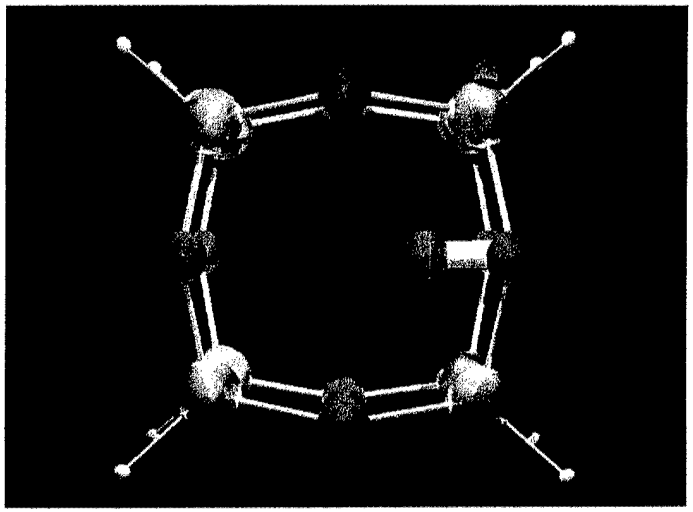
Webb,S.P. and Hammes-Schiffer, S. J. Chem. Phys. 113 (2000), 5214

RESULTS - POSS

Molecular "sieves": preferential capture N_2 vs. O_2?



TS structure of $T_8 + O_2$



T_{10} and T_{12} calculations in progress

HPC requirements: ~50,000 node-hrs, AHPCRC T3E, 256 GB

RESULTS - NLO

B3LYP S_0-T_1 Excitation Energies (in eV)

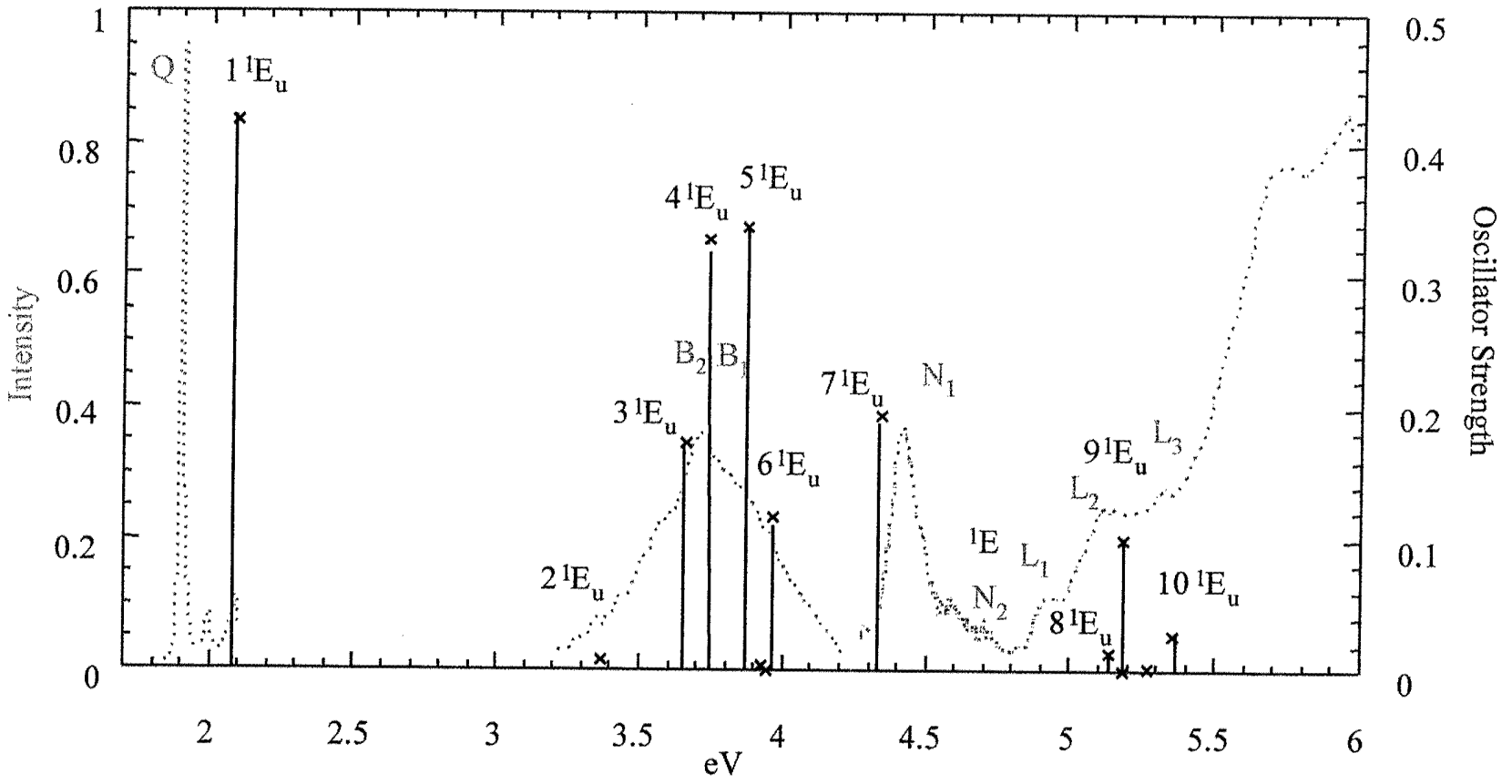
System	6-31G(d)	Error	Exp
Porphyrin (1^3B_{2u})	1.42	0.16	1.58[a]
Zinc Porphyrin (1^3B_{1u})	1.65	0.07	1.72[b]
Tetraphenylporphyrin (1^3B_1)	1.31	0.14	1.45[c]
Zinc Tetraphenylporphyrin(1^3B_1)	1.53	0.06	1.59[d]
Zinc Phthalocyanine (1^3B_{2u})	1.05	0.08	1.13[e]
Zinc Tetrabenzporphyrin (1^3B_{1u})	1.41	0.16	1.57[f]
Phthalocyanine (1^3B_{1u})	1.18	0.06	1.24[g]
Mean Error		0.10	

[a]Gouterman, Khalil, *J. Mol. Spectrosc.* 1974, *53*, 88. (EPA (5:5:2) mixture of ethyl ether to isopentane to ethanol) and 50% ethyl iodide at 77 K) [b]Gradyushko, Tsvirko, *Opt. Spectrosc.* 1971, *31*, 291.(EPA at 77 K) [c]Gouterman, Khalil, *J. Mol. Spectrosc.* 1974, *53*, 88. (EPA at 77 K) [d]Walters et al., *J. Phys. Chem.* 1995, *99*, 1166.(1:1 mixture of ether to ethanol at 77 K) [e]Vincett et al.,K. E. *J. Chem. Phys.* 1971, *55*, 4131. (1-chloronapthalene at 77 K) [f]Bajema, Gouterman, *J. Mol. Spectrosc.* 1971, *39*, 421 (octane at 77 K) [g]McVie et al., *J. Chem. Soc. Faraday Trans. II* 1978, *74*, 1870 (1-chloronapthalene at 77 K)

Nguyen, K. A., Day, P. N., and Pachter, R.: J. Chem. Phys., 110 (1999) 9135
Nguyen, K. A., Day, P. N., and Pachter, R.: J. Phys. Chem. A, 103 (1999) 7378
Nguyen, K. A., Day, P. N., and Pachter, R.: J. Phys. Chem., 104 (2000) 4755
Nguyen, K. A. and Pachter, R., J. Phys. Chem., 104 (2000) 4549

RESULTS - NLO

Comparison with Experiment: ZnPc



HPC Requirements: ~100,000 CPU hours, on SGI O2K + IBM SP3 + SGI O2K @ ASC